Solving the Unimolecular Master Equation with a Weighted Subspace Projection Method

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ABSTRACT: A weighted subspace projection method for solving the unimolecular master equation over a wide range of temperatures and pressures is developed. Sample calculations modeling the dissociation of ethane at 300 K and pressures as low as 0.65 Torr demonstrates the utility of the method in regimes where standard projection methods fail. For the sample calculations the weighted Arnoldi method was able to reliably calculate the smallest eigenvalue of the rate matrix in excellent agreement with calculations using the Nesbet algorithm. Extremely small eigenvalues of the order of -10^{-48} could be calculated without difficulty. The formal equivalence between various weighting schemes and common matrix transformations is shown. The point that merely taking the transpose of the rate matrix can be extremely beneficial is made, commenting on the relationship between the left and right eigenvectors of the rate matrix.
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Introduction

Statistical unimolecular rate theory[1–3] is often the method of choice in the analysis of many reactions important in atmospheric and combustion chemistry. The master equation approach[1,3,4] has been particularly useful in this respect. For a thermally activated unimolecular reaction, the master equation statistically describing the evolution in time of the molecular population as a function of energy is

$$\frac{\partial p(t;E)}{\partial t} = \omega \int_0^\infty P(E|E')p(t;E')\,dE' - \big[\omega + k(E)\big]p(t;E), \quad (1)$$

where $p(t;E)$ is the population distribution, ω is the collision frequency, $P(E|E')$ is the energy transfer kernel describing the probability that a collision involving a molecule at energy E' will leave that molecule at energy E, and $k(E)$ is the microscopic rate constant for unimolecular reaction.

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The most common way to solve this differential-integral equation is to express the equation in terms of a set of discrete energies $\{E_i\}$, transforming eq. (1) into a system of coupled differential equations. The master equation becomes what is known as the energy grained master equation (EGME),[1, 5]

$$\frac{d\underline{p}}{dt} = A\underline{p}, \tag{2}$$

where now the vector $\underline{p}$ is a sampling of the continuous function $p(t; E)$ (so that $p_i = p(t; E_i)$). Note that here the explicit dependence of the vector $\underline{p}$ on time has not been shown. The $n \times n$ matrix A, the rate matrix, is given by

$$A_{ij} = \omega\delta EP(E_i|E_j) \tag{3}$$

for off-diagonal elements and

$$A_{ii} = -\omega\delta E \sum_{j \neq i} P(E_j|E_i) - k(E_i) \tag{4}$$

for elements on the main diagonal, where δE is the energy grain size.

Given some initial population $\underline{p}(0)$, the formal solution of eq. (2) describing the evolution of the population in time is

$$\underline{p}(t) = \exp(At)\underline{p}(0). \tag{5}$$

It is convenient to express eq. (5) in terms of the eigenpairs of the matrix A, i.e., the set of eigenvalues λ_i and corresponding eigenvectors $\underline{x}_i$ that obey

$$A\underline{x}_i = \lambda_i\underline{x}_i. \tag{6}$$

Expanding the initial population in terms of the eigenvectors,

$$\underline{p}(0) = \sum_i a_i\underline{x}_i = \sum_i \underline{x}_i^T\underline{p}(0)\underline{x}_i, \tag{7}$$

eq. (5) is expressed as

$$\underline{p}(t) = \sum_i \exp(\lambda_i t)a_i\underline{x}_i. \tag{8}$$

The numerical solution of the master equation can then be performed by finding the eigenvalues and eigenvectors of the rate matrix A. Note that the formulation given above is for energy grains of equal width. Other discretisations are possible, such as in the Equilibrium Finite Basis Set method.[6]

The matrix A is constrained on physical grounds to be negative semidefinite—its eigenvalues are less than or equal to zero. If this were not the case, i.e., if there existed some eigenvalue $\lambda_i > 0$, then one can see that the solution given by eq. (8) would grow without bound—a physically unacceptable solution. When the EGME is describing a relaxation problem only—that is, when there is no unimolecular reaction and the microscopic rate constant $k(E)$ is zero for all energies—A has exactly one zero eigenvalue. The eigenvector corresponding to the zero eigenvalue represents the Boltzmann thermal equilibrium population

$$f(E) = \rho(E)\exp(-E/k_BT), \tag{9}$$

where T is temperature, k_B is Boltzmann's constant and $\rho(E)$ is the molecular rovibrational density of states. When there is a reaction occurring (i.e., $k(E_i) > 0$ for E_i greater than the reaction threshold energy) the matrix A is negative definite. In this general case the smallest eigenvalue corresponds to the negative of the thermal unimolecular rate constant k_{uni}. This temperature- and pressure-dependent rate constant is most commonly calculated by using an EGME, and can be exceedingly small for low temperatures and pressures. The elements of the eigenvector corresponding to this smallest eigenvalue are always equal to or less than the corresponding elements of the Boltzmann vector $\underline{f}$ defined in the obvious way as $f_i = f(E_i)$.[1]

Clearly, given the complete spectral expansion of eq. (8), the EGME can yield a full description of transient behaviour. However, noting that a given term in the sum in eq. (8) will not contribute significantly to the solution if the $\exp(\lambda_i t)$ term is small, it can be seen the kinetics during different time regimes will tend to be controlled by different parts of the spectrum of A. Indeed, to successfully model the population evolution for times greater than some time τ, one does not require eigenpairs with eigenvalues of absolute value significantly larger than $1/\tau$. This has been exploited recently in developing an approach to isomerization modeling based on a spectrally transformed Lanczos algorithm.[7]

The determination of the required eigenpairs is complicated by many computational details and numerical difficulties. By way of introduction, and to provide motivation for what follows, some of these complicating factors are addressed in the following paragraphs.

As an obvious starting point, one notes that the matrix A is not symmetric. Historically, there has been much more attention payed to methods for calculating the eigenvalues and eigenvectors of Hermitian or symmetric matrices, and these symmetric matrices have various properties that aid in the robustness and stability of algorithms for solving the eigenproblem.[8] Thus, it is usually seen as advantageous to transform the asymmetric matrix A to a symmetric matrix. A suitable transform can be obtained by noting that the $P(E|E')$ function defin-

ing the matrix A must obey detailed balance.[1–4, 9, 10] As a consequence, taking the vector $\underline{f}$ representing the Boltzmann thermal equilibrium population and from it forming the diagonal matrix S,

$$S_{ii} = f_i^{-1/2}, \tag{10}$$

the matrix

$$B = SAS^{-1} \tag{11}$$

is symmetric.[1, 11] Under this similarity transformation the eigenvalues are invariant, and an eigenvector $\underline{x}$ of A and the corresponding eigenvector $\underline{y}$ of B are related by

$$\underline{y} = S\underline{x}. \tag{12}$$

Most work on the numerical solution of the EGME for thermal unimolecular reactions has focused on the symmetric matrix B. In exact algebra the spectrum is invariant under the similarity transformation, so this is the natural approach. However, as has been well documented previously, and will be further discussed below, numerical solution of the eigenvalue problem is prone to catastrophic roundoff error, especially at low temperatures where the thermal unimolecular rate and, hence, the smallest eigenvalue of A can be many orders of magnitude below machine precision. Thus, it is of some interest to consider the effect that the similarity transformation—one of a class of transformations that we shall be exploring—has on the behavior of numerical algorithms for solving the eigenproblem in the presence of roundoff error. This will form a significant part of the analysis presented below, and will lead to the somewhat surprising conclusion that in the presence of roundoff error the symmetric variant of the EGME eigenproblem is not necessarily the optimal one for numerical solution.

The eigenproblems to be solved are usually large, making iterative solution algorithms whose basic operation is the formation of a matrix-vector product of central importance. Consider now the effect of roundoff error on the matrix-vector product. The normalization requirement of the probability function $P(E|E')$,

$$\int_0^\infty P(E|E')\,dE = 1, \tag{13}$$

forces the off-diagonal elements of A to be smaller than $\omega\delta E$. The diagonal elements are all negative, no smaller than approximately $-\omega$ and, due to the $k(E)$ term in eq. (4), may be very large. This potentially extreme diagonally dominant character of the matrix A has the consequence that it may well be impossible to accurately compute a matrix-vector product with an eigenvector (or even an approximation thereto) corresponding to an eigenvalue that is small in comparison with machine precision. Such a matrix-vector product relies on calculating the difference between a single large term arising from the diagonal matrix entry and a sum of small terms arising from the off-diagonal matrix entries. The difference between these two numbers is proportional to the corresponding eigenvalue, so for very small eigenvalues very high levels of numerical precision would be required to gain an accurate value for the matrix-vector product. Such high precision is simply not available in most computing environments. The inability to form these matrix-vector products applies almost equally as much to the symmetric matrix B, and prevents one from using the residual norm, $\|A\underline{x} - \lambda\underline{x}\|$ or $\|B\underline{y} - \lambda\underline{y}\|$, as a measure of the quality of eigenpairs with small eigenvalues.

Some ingenious methods have been developed specifically to circumvent these difficulties and find the troublesome eigenpair corresponding to the smallest eigenvalue.[1, 12–14] Perhaps the most successful and widely used of these is the adapted Nesbet method[15] of Gilbert and coworkers.[12, 13] There are several features of this method that are worthy of note. First, the matrix-vector product is carefully constructed, using both the mathematical structure and special properties of the matrix B and a rescaled representation $\underline{h}$ of the desired eigenvector $\underline{y}$,

$$h_i = y_i/f_i^{1/2} = x_i/f_i, \tag{14}$$

to minimize as far as possible numerical error. Second, recognizing that numerical evaluation of the smallest eigenvalue λ_1 from the corresponding eigenvector $\underline{y}_1$ (or equivalently $\underline{x}_1$) via the Rayleigh Quotient expression,

$$\lambda_1 = \frac{\underline{y}_1^T B \underline{y}_1}{\underline{y}_1^T \underline{y}_1} = \frac{\underline{x}_1^T A \underline{x}_1}{\underline{x}_1^T \underline{x}_1}, \tag{15}$$

is hopelessly inaccurate due to roundoff error, the eigenvalue is estimated instead from the expression[16]

$$\lambda_1 = \frac{\sum_j k(E_j) h_j^1 f_j}{\sum_j h_j^1 f_j} = \frac{\sum_j k(E_j) y_j^1 f_j^{1/2}}{\sum_j y_j^1 f_j^{1/2}} = \frac{\sum_j k(E_j) x_j^1}{\sum_j x_j^1}, \tag{16}$$

where x_j^1 is the jth element of $\underline{x}_1$, and similarly for $\underline{y}_1$ and $\underline{h}_1$. Finally, by virtue of its being an iterative single-vector update algorithm, the Nesbet method sidesteps the loss of accuracy (incurred by virtually all basis set methods) associated with the evaluation of matrix elements and subsequent matrix diagonalisation. A correction vector is estimated and

added directly to the existing approximate solution, refining the eigenvector until the eigenpair [with the eigenvalue estimate coming from eq. (16)] converges, avoiding problems associated with widely varying magnitudes for different regions of the correction vector.

The success of the Nesbet algorithm indicates that, provided one is careful, the limitations on accuracy in forming the matrix-vector product do not prevent the accurate calculation of an eigenvalue—and, hence, a thermal unimolecular rate constant—which is many orders of magnitude below machine precision. Although this is suitable for calculating a unimolecular dissociation rate constant (or the stabilization rate constant for the reverse reaction), it provides only part of the information that is necessary to deal with problems in which the relaxation is an intrinsic part of the kinetics, such as product branching ratios in chemical activation reactions. An obvious approach is to suggest a hybrid method. For example, first the troublesome eigenpair with the lowest eigenvalue can be calculated with the Nesbet method. Following this, one could attempt to compute the remaining eigenpairs with another iterative method such as Lanczos or Davidson subspace projection,[17–20] incorporating deflation of the subspace with the lowest-lying eigenvector from the Nesbet calculation. In trial calculations, however, this approach has been found to be problematic. Attempts at deflation of the Lanczos or Davidson subspaces with the Nesbet eigenvector persistently failed, with inaccurate copies of the Nesbet eigenvector reappearing to contaminate the subspace.[21] As if this were not enough, the problem is exacerbated in the case of chemical reactions involving rapid interconversion between multiple deep-well isomeric species, because in these cases there are multiple small eigenvalues controlling the long-time kinetics.

To surmount the difficulties summarised above, an eigenproblem solution method that can accurately compute all of the physically relevant eigenpairs of the EGME is needed. At the heart of this challenge is the question of how to make subspace projection methods (such as the Lanczos, Arnoldi, or Davidson methods[17–20]) sensitive to the eigenpair(s) of the EGME with small eigenvalues.

This article explores the potential advantages of a weighted inner product within an orthogonal subspace projection method. It will be seen that (within reasonable limits) the judicious choice of a weight function does indeed restore sensitivity to the extremely small eigenvalues. This has allowed the precise calculation of eigenpairs with eigenvalues of the order of 10^{-48}, with subspace projection methods that would otherwise fail miserably. The following section expands upon some of the ideas mentioned above in developing this new weighted inner product subspace projection (WIPSP) approach to the EGME. Relations between the WIPSP method and a class of similarity transformations—including the symmetrisation of the original matrix A to formulate the eigenproblem with the symmetric matrix B—will be derived, leading to the conclusion that, in the presence of roundoff error, similarity transformations of the type indicated in eqs. (11) and (12) have a profound effect on the numerical performance of subspace projection approaches to the solution of the eigenproblem. Numerical application to several versions of a test problem, some more theoretical development and conclusions follow. The subspace projection method developed primarily is the Arnoldi method,[8, 18] although the Davidson method[19, 20] is also investigated.

The Weighted Arnoldi Method

The first observation that motivates the use of a weight function in the solution of the EGME comes from eq. (16). This formula reveals that, because $k(E)$ is zero below the reaction threshold energy E_0, the eigenvalue, in effect, depends only on elements of the eigenvector corresponding to energies above the reaction threshold. Now, in the Boltzmann distribution $f(E)$ the population at energies lying above the reaction threshold is usually dozens of orders of magnitude smaller than the population at average thermal energies. Recalling that the eigenvector corresponding to the smallest eigenvalue is essentially equal to the Boltzmann distribution at lower energies, but has elements of smaller magnitude than $f(E)$ near and above E_0, eq. (16) implies that the elements of the eigenvector vital for determining the eigenvalue are many orders of magnitude smaller than the elements of the eigenvector on which the eigenvalue has no real dependence.

Consider the implications of this on the behavior of orthogonal subspace projection methods. These methods rely on finding approximations $\underline{x}$ to an eigenvector that lies within some subspace $\mathcal{S} \subset \mathbb{R}^n$ and satisfy the Galerkin condition,[18]

$$\langle \underline{r}, \underline{v} \rangle = 0, \qquad \forall \underline{v} \in \mathcal{S}, \tag{17}$$

where the vector $\underline{r}$ is the residual vector,

$$\underline{r} = A\underline{x} - \tilde{\lambda}\underline{x}. \tag{18}$$

Projection methods are defined by the subspace $\mathcal{S}$ used, with different methods utilizing different

subspaces and subspace generation techniques. The equation that is being solved, eq. (17), amounts to a series of inner product evaluations over a set of vectors. Consider then an approximate eigenvector $\underline{x} \in \mathcal{S}$ corresponding to the smallest eigenvalue. Given that the system is being solved in finite precision arithmetic, the residual vector $\underline{r}$ will likely be comprised of non-zero numerical noise at energies well below threshold, where the approximation $\underline{x}$ is essentially equal to $\underline{f}$ (as is the true eigenvector). On the other hand, at energies close to or above threshold, $\underline{r}$ carries important information about the error in the approximate eigenvector, because it is in this region that the approximate eigenvector deviates most significantly from the true eigenvector. Although the relative error in the eigenvector is much greater near and above threshold, the absolute magnitude of the elements of $\underline{r}$ at low energies—the numerical noise—is still many orders of magnitude larger than the magnitude of the significant elements of $\underline{r}$ corresponding to energies above threshold. In this situation, the inner products of eq. (17) will be totally dominated by the numerical noise, and any useful information is lost. Hence, as eq. (17) can only be solved to within machine precision, the Galerkin condition can be totally insensitive to relative errors in the vital elements of $\underline{x}$ corresponding to energies above the reaction barrier.

Now consider shifting the calculation into an inner product space in which the inner product is a weighted Euclidean inner product. If the elements of the vectors corresponding to energies above the reaction barrier are given a much higher weight than those significantly below the barrier, the Galerkin condition—and hence the projected matrix in the subspace projection method—can regain sensitivity to the vital region of the energy scale near and above the reaction barrier. Noting again that the troublesome eigenvector corresponding to the smallest eigenvalue is similar in shape to the Boltzmann distribution $f(E)$, it would seem that an appropriate weighting for this new inner product would have a shape broadly similar to $1/f(E)$.

It is instructive to examine the mechanism of the subspace projection. Forming the set of weights w_i into a matrix,

$$X = \mathrm{diag}(w_1, w_2, \ldots, w_n), \tag{19}$$

the weighted Euclidean inner product becomes

$$\langle \underline{u}, \underline{v} \rangle_X = \sum_i u_i w_i v_i = \underline{u}^T X \underline{v}. \tag{20}$$

For the standard eigenvalue problem, eq. (6), the projection problem becomes finding an eigenvector estimate lying within the m-dimensional subspace $\mathcal{S}$ that satisfies eq. (17). Constructing an $n \times m$ matrix V whose columns $\underline{v}_k$ form a particular basis for the subspace $\mathcal{S}$

$$\mathcal{S} = \mathrm{span}(\underline{v}_1, \underline{v}_2, \ldots, \underline{v}_m), \tag{21}$$

solving eq. (17) entails finding some coefficient vector $\underline{c} \in \mathbb{R}^m$ for which the eigenvector estimate

$$\underline{x} = V\underline{c} \tag{22}$$

yields a residual vector $\underline{r}$ orthogonal to the subspace $\mathcal{S}$. Combining eqs. (17), (21), and (22) with the weighted inner product, the Galerkin condition that must be satisfied is

$$\left\langle AV\underline{c} - \tilde{\lambda} V\underline{c}, \underline{v}_k \right\rangle_X = 0, \qquad \underline{k} = 1, \ldots, m. \tag{23}$$

Satisfying this condition is equivalent to solving the small projected eigenproblem

$$V^T X A V \underline{c} = \tilde{\lambda} V^T X V \underline{c}. \tag{24}$$

The generalized eigenproblem in eq. (24) can be transformed to a standard eigenproblem by requiring that the subspace $\mathcal{S}$ be expressed in an X-orthonormal basis, so that

$$V^T X V = I. \tag{25}$$

Eq. (24) becomes

$$H_{A(X)}\underline{c} = \tilde{\lambda}\underline{c}, \tag{26}$$

where the $m \times m$ projected matrix

$$H_{A(X)} = V^T X A V \tag{27}$$

has been identified from eq. (24). Usually for subspace projection methods $m \ll n$, so that the projected eigenproblem in eq. (26) is indeed small, and can easily be solved by direct methods. Note that when no weighting is applied the formulation of the projected matrix is

$$H_A = V^T A V. \tag{28}$$

In other words, $H_{C(X)}$ is the notation used here for the projection of some matrix C onto the subspace with an inner product weighted by the diagonal matrix X, while H_C gives the unweighted projection.

The projected problem expressed in eq. (24) corresponds exactly to the projected problem obtained by applying the unweighted Galerkin condition for an eigenvector estimate within the subspace $\mathcal{S}$ to the generalized eigenproblem

$$XA\underline{x} = \lambda X\underline{x}. \tag{29}$$

This shows that solving the standard eigenvalue problem, eq. (6), with a weighted inner product, is

not only formally equivalent to solving the preconditioned version in eq. (29), but that projecting the two problems onto the same subspace $\mathcal{S}$ will produce identical eigenpair estimates. This result holds even in the presence of roundoff error.

It remains to choose a suitable subspace projection method for trialing the weighted inner product (WIP) approach. The Lanczos method[8, 17, 22] is a common projection method used for symmetric matrices, where the subspace being projected onto is a Krylov subspace,

$$\mathcal{K}^{(m)}(B, \underline{v}) = \text{span}\left(\underline{v}, B\underline{v}, B^2\underline{v}, \ldots, B^{m-1}\underline{v}\right). \quad (30)$$

However, the Lanczos method cannot be implemented within a weighted inner product space, as B is no longer symmetric with respect to the inner product,

$$\langle \underline{u}, B\underline{v}\rangle_X \neq \langle \underline{v}, B\underline{u}\rangle_X. \quad (31)$$

Thus, the closely related but more expensive Arnoldi method[8, 18] must be used. The Arnoldi method also projects the matrix onto a Krylov subspace, and is formally equivalent to the Lanczos method when applied to symmetric matrices. However, weighted or otherwise, the Arnoldi method is applicable to both symmetric matrices, such as B, and nonsymmetric matrices, such as A.

It is expensive and inefficient to build the Krylov subspace required for the Arnoldi method by explicitly applying powers of the matrix as per the definition, eq. (30). Rather, to add the vector $A^m\underline{v}$ to the basis of the subspace $\mathcal{K}^{(m)}(A, \underline{v})$ to form the subspace $\mathcal{K}^{(m+1)}(A, \underline{v})$ note that because the basis vector $\underline{v}_m \in \mathcal{K}^{(m)}(A, \underline{v})$, one can write

$$\underline{v}_m = \rho_{m-1}(A)\underline{v}, \quad (32)$$

where $\rho_{m-1}(A)$ is a polynomial of degree exactly $m-1$. Then[17]

$$\begin{aligned}\text{span}(\underline{v}_1, \ldots, \underline{v}_m, A\underline{v}_m) &= \text{span}\left(\underline{v}_1, \ldots, \underline{v}_m, A\rho_{m-1}(A)\underline{v}\right)\\ &= \text{span}\left(\underline{v}_1, \ldots, \underline{v}_m, A^2\rho_{m-2}(A)\underline{v}\right)\\ &= \text{span}\left(\underline{v}_1, \ldots, \underline{v}_m, A^m\underline{v}\right)\\ &= \mathcal{K}^{(m+1)}(A, \underline{v}). \end{aligned} \quad (33)$$

Hence, to iteratively build the Krylov subspace up to any dimension m requires only $m-1$ matrix-vector multiplies, rather than the $(m^2-m)/2$ implied by eq. (30). One notes that applying the Arnoldi method with a weighted inner product merely changes the coefficients of the polynomials $\rho_i(A)$ in eq. (33). The subspace being projected onto remains the same.

At the mth step of the iterative subspace building procedure, the vector $A\underline{v}_{m-1}$ added to the basis V is orthonormalised against the existing $m-1$ basis vectors $\underline{v}_1, \ldots, \underline{v}_{m-1}$. This is achieved with the Modified Gram–Schmidt procedure[8] applied with the weighted inner product. The resultant vector becomes the new basis vector, $\underline{v}_m$. So while the subspace $\mathcal{S} \equiv \mathcal{K}^{(m)}(A, \underline{v})$ being projected onto does not alter for the WIP Arnoldi method, the set of basis vectors that the subspace is being represented by does change to accommodate the orthonormality condition, eq. (25). The fact that the Arnoldi method employs a Krylov subspace means that the projected matrix is upper Hessenberg (zeros on all lower diagonals bar the first below the main diagonal), and the remaining element of this matrix, the last element of this first subdiagonal, can still be obtained as the final normalizing factor in the Gram–Schmidt procedure.[18] The projected matrix H is changed by both the change in the basis vectors and the fact that the new inner product alters the effective definition of the matrix element [eq. (27) as opposed to eq. (28)].

After setting a weight function, forming the weights into a diagonal matrix X [as per eq. (19)] and specifying a subspace seed vector $\underline{v}_1$ with $\|\underline{v}_1\|_X = 1$, the WIPSP Arnoldi method may be summarized by the following pseudocode:

$$\begin{array}{l}
\underline{w} := A\underline{v}_1\\
h_{1,1} := \langle \underline{v}_1, \underline{w}\rangle_X\\
\underline{w} := \underline{w} - h_{1,1}\underline{v}_1\\
\text{for } k := 2, 3, \ldots\\
\quad h_{k,k-1} := \|\underline{w}\|_X\\
\quad \underline{v}_k := h_{k,k-1}^{-1}\underline{w}\\
\quad \underline{w}_k := B\underline{v}_k\\
\quad \text{for } i := 1, 2, \ldots, k\\
\quad\quad h_{i,k} := \langle \underline{v}_i, \underline{w}\rangle_X\\
\quad\quad \underline{w} := \underline{w} - h_{i,k}\underline{v}_i\\
\quad \text{end}\\
\text{end}
\end{array} \quad (34)$$

After each iteration of the outer loop there are k basis vectors $\underline{v}_j$ available and the $k \times k$ matrix $H_{A(X)}$ is formed by the elements h_{ij} (with $h_{ij} = 0$ for $i > j+1$). After any particular iteration the projected eigenproblem eq. (26) can be solved by a direct method (such as the QR method) to obtain the eigenvectors $\underline{x} = V\underline{c}$.

The algorithm presented in (34) represents the basic procedure with a single orthoganization step. In all of the calculations presented here a reorthoganalization was utilized, as this improved the numerical stability of the methods.[23] The reorthoganalization step simply repeats the Modified Gram–Schmidt procedure [the inner loop in (34)] without storing the $\langle \underline{v}_i, \underline{w}\rangle_X$ inner product terms. The general behav-

ior of the methods remain the same with or without the reorthoganalization step.

Similarity Transformations and Implicit Weighting

Intriguingly, the similarity transformation leading to the symmetrisation of the rate matrix, eq. (11), is implicitly introducing a weighting to the master equation. To see this, note first that converting the master equation from the continuum form in eq. (1) to the discrete solution specified by eqs. (6) and (8) can be viewed as a projection of the problem from an infinite dimensional function space to the n dimensional real space $\mathbb{R}^n$ spanned by the columns of the identity matrix I. The similarity transform of the eigenproblem from A to B can then be viewed as changing the expression of the master equation from the grid basis I to the grid basis S^{-1}. Start with the eigenproblem weighted or preconditioned by the weight function

$$W = S^2, \tag{35}$$

thus,

$$WA\underline{x} = W\lambda\underline{x}. \tag{36}$$

Change basis from the original grid basis represented by the columns of I to a new grid basis represented by the columns of S^{-1} (i.e., the new grid basis vector at energy E_i is proportional to $f_i^{1/2}$). An eigenvector $\underline{x}$ is now to be expressed as a linear combination of the columns of S^{-1},

$$\underline{x} = S^{-1}\underline{y}, \tag{37}$$

which is equivalent to eq. (12). Equation (36) now becomes

$$WAS^{-1}\underline{y} = W\lambda S^{-1}\underline{y}. \tag{38}$$

Projection onto both sides of eq. (38) from the left with the basis S^{-1} then yields

$$S^{-1}WAS^{-1}\underline{y} = \lambda S^{-1}WS^{-1}\underline{y} \tag{39}$$

$$\Leftrightarrow SAS^{-1}\underline{y} = \lambda\underline{y} \tag{40}$$

$$\Leftrightarrow B\underline{y} = \lambda\underline{y} \tag{41}$$

by the definition of W. Thus, the similarity transformation from the nonsymmetric eigenproblem involving A to the symmetric eigenproblem involving B corresponds to a global weighting or preconditioning of the eigenproblem by the diagonal matrix W. A natural question, closely related to this exploration of WIPSP methods, is therefore, whether this type of similarity transformation also has an effect on the numerical performance of the subspace projection methods.

Pursuing the same line further, another global grid basis transformation can prove useful. A property of the rate matrix A not often recognized is that applying the similarity transform of S once more to B yields

$$SBS^{-1} = WAW^{-1} = A^T. \tag{42}$$

Using this property, the eigenvalue problem, eq. (6), gives

$$W^{-1}A^TW\underline{x} = \lambda\underline{x} \tag{43}$$

$$\Leftrightarrow A^TW\underline{x} = \lambda W\underline{x} \tag{44}$$

$$\Leftrightarrow A^T\underline{h} = \lambda\underline{h}, \tag{45}$$

where the vector $\underline{h}$ is defined as

$$\underline{h} = W\underline{x}. \tag{46}$$

Analogous to the derivation of eqs. (36) through (41) above, the similarity transformation leading to eq. (45) can be regarded as implicitly introducing a weighting W^2 into the EGME via a global transformation from the grid basis I to a new grid basis represented by the columns of W^{-1}.

Equations (42) to (45) show that the right eigenvectors $\underline{x}$ of the matrix A are related to the left eigenvectors of A by eq. (46). Because the elements of the diagonal weight matrix W are proportional to $\underline{f}^{-1}$, eq. (46) is equivalent to eq. (14), meaning the vector $\underline{h}$ expresses the eigenvector in the same way as does the adapted Nesbet method discussed above. It remains to point out that—unlike $\underline{x}_1$ and $\underline{y}_1$—the low-lying eigenvector $\underline{h}_1$ does not suffer from the malaise of having elements spanning dozens of orders of magnitude. As will be apparent in the results of the next section, this fact leads to the surprising conclusion that the *asymmetric* eigenvalue problem of eq. (45) is far better conditioned for the application of subspace projection methods than the symmetric variant, eq. (41), which has traditionally been the focus of attention in numerical solutions of the EGME.

Sample Calculations. 1. The ECT Kernel

Several sets of sample calculations were performed to test the performance of the WIP Arnoldi method with differently weighted inner products on the three different versions of the rate matrix (A, B, and A^T). The model used for the calculations

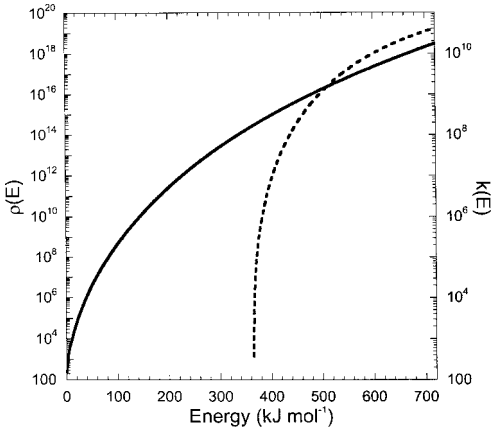

FIGURE 1. Density of states (—) and microscopic rate constants (- - -) used for ethane model.

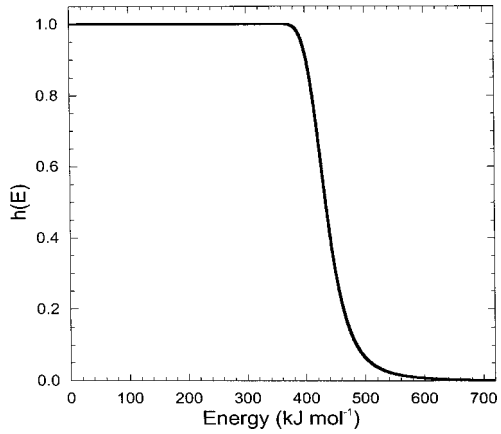

FIGURE 2. Eigenvector of the matrix A derived from the ECT kernel expressed as $\underline{h}$, a fraction of the Boltzmann population.

described here was a model describing the dissociation of ethane into two methyl fragments,

$$C_2H_6 \rightarrow 2CH_3. \tag{47}$$

Two flavors of the energy transfer kernel $P(E|E')$ were used, one derived from Ergodic Collision Theory (ECT)[24] and one using an exponential-down model for the energy transfer. The ECT model is generally considered to be a limiting case for perfectly efficient collisions and has a broad profile. Although exponential-down model has little rigorous theoretical basis, it is a more common approximation to the true energy transfer probability function and is considered a more realistic model, principally because it allows the empirical modeling of weak energy transfer. The calculations using the ECT model are dealt with in this section, whereas the exponential-down model calculations are treated in the following section.

The density of states of ethane and the microscopic rate constant used are shown in Figure 1. This density of states and set of microscopic rate constants have been used previously for modeling this reaction.[25] The matrix A was constructed for a temperature of 300 K and a collision frequency ω of 8×10^7 s^{-1}, corresponding to a pressure of approximately 6.5 Torr.

The weighted Arnoldi method was applied to the original rate matrix A, the symmetrized version B, and the transpose A^T. The Arnoldi method was applied with four different inner products, being the unweighted Euclidean inner product and three weighted inner products. The weighted inner products used the weightings provided by the matrices S and W, previously defined in eqs. (10) and (35), and the matrix W^2. The four inner products and three matrices gave a total of 12 methodic variants. The matrices constructed were 600×600, spanning an energy range from zero to 720 kJ mol^{-1}. As is apparent from the rate constants shown in Figure 1, the reaction barrier for this reaction is 365 kJ mol^{-1} high.

Applying the Nesbet algorithm to this system yielded unimolecular rate constant estimates converging very quickly (within two to three iterations) to 2.7025×10^{-48} s^{-1}. The corresponding eigenvector, expressed in terms of the rescaled vector $\underline{h}$, is shown in Figure 2. In fact, at the pressure and temperature considered, the system is very close to the high-pressure limit, which explains the speed of convergence for the Nesbet method. However, because the eigenvalue is very small, this is an extremely demanding test for any subspace projection approach. Despite this, the weighted Arnoldi method was able to produce eigenvalue estimates converging to this value with high accuracy, as shown in Figure 3. In contrast, the unweighted Arnoldi method applied to both A and B failed to converge. Note that although it appears from Figure 3 that applying the unweighted Arnoldi method to the matrix A performed reasonably in the first few iterations, the actual eigenvector estimates produced in these iterations were unacceptable, becoming large and oscillatory.

One of the most striking features of Figure 3 is that the eigenvector estimates produced by applying the unweighted Arnoldi method to the matrix A^T, the Arnoldi method weighted with W to the matrix B and the Arnoldi method weighted with W^2 to the matrix A produce successive eigenvalue estimates that are indistinguishable on the scale of

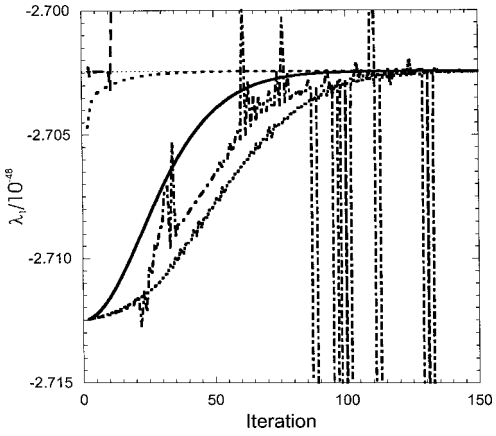

FIGURE 3. Successive eigenvalue estimates calculated from eq. (16) for WIP Arnoldi methods applied to ECT-derived EGME matrices. Eigenvalue estimates from unweighted Arnoldi and Arnoldi weighted by S on A coincide (- - -), as do eigenvalue estimates from unweighted Arnoldi on A^T, Arnoldi weighted with W on B and Arnoldi weighted with W^2 on A (—) and Arnoldi weighted with W applied to A^T and Arnoldi weighted with W^2 applied to B (- · -). Other data shown is for Arnoldi weighted by S on B (· · ·) and A^T (····). Light dotted line shows converged value.

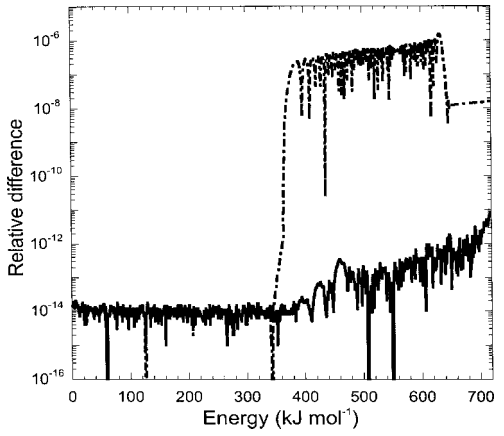

FIGURE 4. Relative difference between the eigenvector estimate corresponding to the smallest eigenvalue produced by the Arnoldi method applied to the matrix A^T and the corresponding vector produced by the Nesbet method after 150 (- · -) and 300 iterations (—). Relative difference between the A^T derived vector and the corresponding eigenvector estimates of the W weighted Arnoldi method applied to the matrix B and the W^2 weighted Arnoldi method applied to the matrix A was of order 10^{-12} or less. ECT kernel.

Figure 3. Additionally, these three variants appear from Figure 3 to be some of the most successful variants tried, outperformed in speed of convergence by the S-weighted Arnoldi method on B only. As Figure 4 shows, the eigenvector estimates produced by these three variants agree well with the Nesbet method, with the maximum relative difference being of the order 10^{-6} after 150 iterations. The agreement continues to improve with further iterations, so that the difference is well below 10^{-11} everywhere after 300 iterations. These three variants of the weighted Arnoldi method turn out to have an intrinsic equivalence, as do several others. This shall be addressed in detail in a following section.

The eigenvalue estimates from applying the unweighted Arnoldi method to the A matrix and applying the S-weighted Arnoldi method to the A matrix are so similar that they are also represented by a single curve in Figure 3, as are the eigenvalue estimates from applying the W-weighted Arnoldi method to A^T and the W^2-weighted Arnoldi method to B. The latter case demonstrated a reasonable amount of instability, at some iterations producing wildly inaccurate eigenvector estimates and corresponding eigenvalues. This behavior shows up in Figure 3 as the vertical lines for more than 85 iterations, which connect reasonable and unreasonable eigenvalue estimates. Of the five remaining variants, only the results from two are shown in Figure 3. The three variants not shown in Figure 3 are unweighted Arnoldi on B, W-weighted Arnoldi on A, and W^2-weighted Arnoldi A^T. These three variants produced successive eigenvalue estimates that were extremely oscillatory and did not converge.

The eigenvalue estimates produced by applying the Arnoldi method weighted with S to the B matrix converge very quickly to the converged value obtained with the Nesbet method. After 150 iterations the eigenvalues produced by these two methods agree to 10 significant figures. The corresponding eigenvector, on the other hand, becomes oscillatory towards the high energy end, so that above around 520 kJ mol^{-1} the eigenvector becomes meaningless.

The two remaining variants shown in Figure 3, which appear to converge to the correct eigenvalue, are the Arnoldi method weighted by the matrices W and W^2 applied to the A^T matrix. In this case, the eigenvalue and eigenvector are of similar quality, differing from the Nesbet counterparts by at most a factor of 10^{-4}, and generally by a considerably smaller factor for the eigenvector.

Recalling that the original aim was to construct a method capable of producing all of the physically relevant eigenpairs to satisfactorily solve eq. (8), now consider larger eigenvalues and their associated eigenvectors. The situation for these eigenpairs

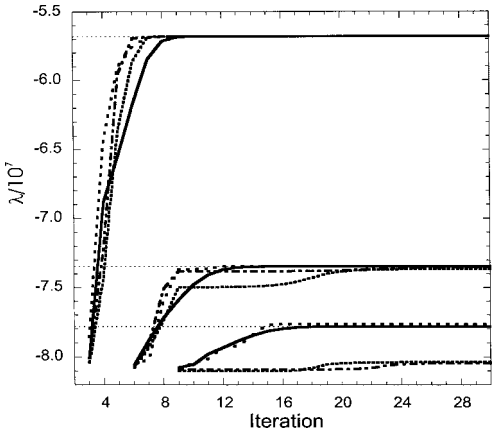

FIGURE 5. Successive eigenvalue estimates for the third (around -5.7×10^7), sixth (around -7.3×10^7) and ninth (around -7.8×10^7) smallest eigenvalues. Unweighted Arnoldi on A (—), unweighted Arnoldi on B (- - -), S weighted Arnoldi on A (· · ·) and W weighted Arnoldi on A (····). Calculated as a Ritz value. ECT kernel. Light dotted lines show converged values.

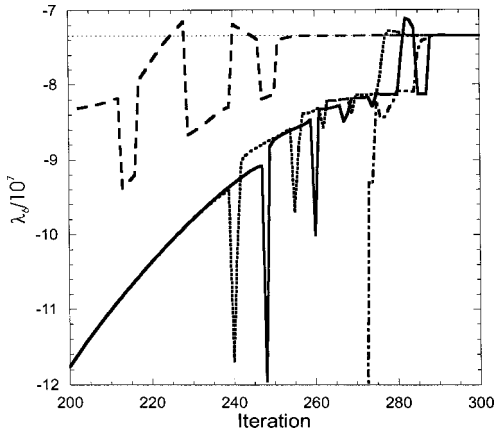

FIGURE 6. Successive eigenvalue estimates for the sixth smallest eigenvalue. Unweighted Arnoldi on A^T (—), S weighted Arnoldi on B (- - -) and A^T (- · -) and W weighted Arnoldi on B (····). Successive eigenvalue estimates for W^2 weighted Arnoldi on A are nearly coincident with those for W weighted Arnoldi on B. Calculated as a Ritz value. ECT kernel. Light dotted line shows converged value.

is considerably different. As examples, examine the third, sixth, and ninth smallest eigenvalues. Such eigenpairs are required to access transient behavior at middle-term time scales (e.g., see refs. 7 and 26). These eigenvalues are determined most consistently by the Arnoldi method unweighted or weighted with S applied to the A matrix, as shown in Figure 5. The unweighted Arnoldi method applied to the matrix B and the W-weighted Arnoldi method applied to A also converge quickly for the lower eigenvalues, although eigenvalues above the sixth lowest (and to some extent the sixth lowest itself) are slow to converge, taking up to 200 iterations to converge to a reasonable extent. If the calculations are performed without the second orthogonalization step on the subspace basis these eigenvalues suffer badly from ghosting,[17, 18, 22] as the iterations are continued after convergence.

Other variants were found to be capable of calculating the required eigenvalues in this case, but at a higher cost. Applying the a moderate amount of weighting to the method (either to the matrix by using A^T, to the Arnoldi method by weighting with W^2 or a partitioning between the two, such as weighting the Arnoldi method by W and using the B matrix) allows the higher eigenvalues to converge in a number of iterations approaching 300. Examples of the convergence behavior are shown in Figure 6 for the sixth smallest eigenvalue. Applying too much weighting to the method (such as applying an Arnoldi method weighted by W or W^2 to the A^T matrix) meant that the method did not converge in 300 iterations.

Any subspace projection method can, in principle, be implemented with a weighted inner product in this fashion. The Davidson method[19, 20] was tested with the same weightings as the Arnoldi method above. For the test system with the ECT kernel, the traditional unweighted Davidson method failed to converge to the smallest eigenpair. Two of the weighted variants, on the other hand, gave superior convergence to the smallest eigenpair. The eigenpair estimate produced by the Davidson method weighted by S applied to B converged to the same eigenpair produced by the Nesbet method after just one iteration. The eigenpair estimate produced by the Davidson method weighted by W applied to B converged after 45 iterations, after appearing to diverge for the first 30 iterations and then oscillating for around 15 iterations. No other weighting variant converged in 300 iterations. Critically for the method, no eigenpair other than the smallest converged in 300 iterations for any of the weighting variants tested.

Sample Calculations. 2. Exponential-Down Kernels

The Exponential-down model for energy transfer has a much narrower and more strongly peaked probability profile than the ECT model. Energy

transfer to a lower energy is described by a single exponential, and can be characterized by a single parameter $\langle \Delta E \rangle_{\text{down}}$. In this model, the probability density for upward or energy gaining transfers are determined from the exponential downward probabilities by applying the condition of detailed balance.

The 12 weighted Arnoldi method variants discussed in the previous section were applied to several different exponential-down–based energy transfer kernels for the same ethane dissociation reaction. These kernels varied in the characteristic $\langle \Delta E \rangle_{\text{down}}$ parameter used, with this parameter taking the values 500 cm^{-1}, 300 cm^{-1}, 100 cm^{-1}, and 75 cm^{-1}. Generally, the calculations were conducted for systems at the same temperature and pressure as for the ECT case—300 K and 6.5 Torr. The narrower the kernel (that is, the lower the $\langle \Delta E \rangle_{\text{down}}$ parameter), the less efficient the energy transfer being modeled. This effectively makes the calculation at 6.5 Torr a calculation further down into the fall-off region.

The behavior of the 12 variants when applied to the rate matrices derived from the exponential-down kernels was generally similar to that observed for the ECT kernel case. There was an observed trend for a larger number if iterations required for convergence as the width of the kernel profile was decreased. This trend applied to the Nesbet method equally, with up to 250 iterations being required in some cases to achieve reasonable convergence.

The variant that converged fastest to the smallest eigenvalue was again the Arnoldi method weighted by S applied to the B matrix, but, as in the ECT case, the eigenvector was far from convergence for the elements corresponding to high molecular energies. Two of the three variants equivalent to unweighted Arnoldi on A^T (that one and the W weighted Arnoldi method applied to B) produced coincident eigenvalue estimates as a function of iteration number as expected in all cases studied, and were once more stable and reliable. The third variant formally equivalent to these two, the Arnoldi method weighted by W^2 applied to the A matrix, produced coincident eigenvalue estimates for a number of iterations before diverging. Examining the successive eigenvector estimates shows that in this case as the high energy elements of the eigenvector were converging, the elements corresponding to the low energy elements (which were originally correct as the seed vector for the Krylov subspace was a suitably transformed Boltzmann vector f) started to diverge. In this case, it seems that the weighting was causing the high-energy

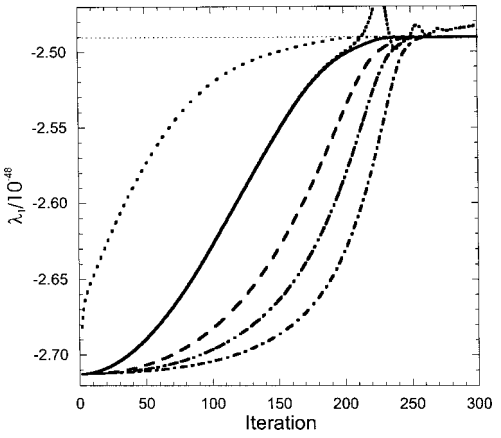

FIGURE 7. Successive eigenvalue estimates for the smallest eigenvalue of the rate matrix derived from the exponential-down model with $\langle \Delta E \rangle_{\text{down}} = 100\ \text{cm}^{-1}$. Unweighted Arnoldi on A^T and W weighted Arnoldi on B (—), S weighted Arnoldi on B (· · ·) and A^T (- - -), W weighted Arnoldi on A^T and W^2 weighted Arnoldi on B (- · · -) and W^2 weighted Arnoldi on A (·—·) and A^T (- · -). Calculated as a Ritz value. Light dotted line shows converged value.

elements to dominate the low-energy ones in the inner products in the Galerkin condition [eq. (17)], a situation exactly opposite the normal behavior of unweighted subspace projection methods for these systems. The convergence behavior for the smallest eigenvalue is summarized in Figure 7 for the representative $\langle \Delta E \rangle_{\text{down}} = 100\ \text{cm}^{-1}$ case.

In all cases, four of the variants were able to converge the larger eigenvalues. These were the same variants that were the most successful in the ECT kernel case—the unweighted Arnoldi method applied to B and the Arnoldi method applied to the A matrix with no weighting, and weighted by S and W. However there were some curious trends when all of the variants were considered. Generally speaking, as the energy transfer kernel was narrowed (by reducing the $\langle \Delta E \rangle_{\text{down}}$ parameter), these successful variants took longer to converge, particularly the traditional unweighted Arnoldi method applied to the symmetric B matrix. On the other hand, the other, more heavily weighted variants became more stable. Despite this increased stability, no other variant was able to converge even the second smallest eigenvalue within 300 iterations in any case studied, as Figure 8 demonstrates.

The convergence behavior of the 12 variants was investigated as the collision frequency was changed (corresponding to a change in pressure) for the exponential-down kernel with $\langle \Delta E \rangle_{\text{down}} =$

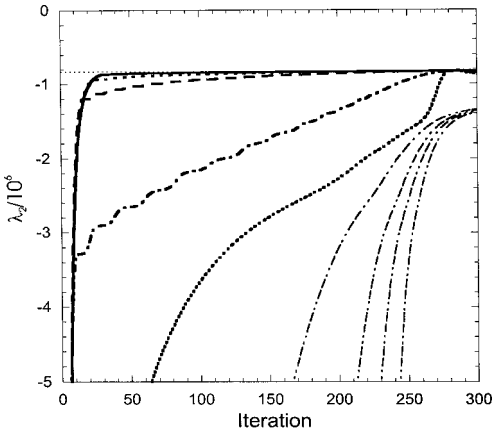

FIGURE 8. Successive eigenvalue estimates for the second smallest eigenvalue of the rate matrix derived from the exponential-down model with $\langle \Delta E \rangle_{\text{down}} = 75\ \text{cm}^{-1}$. Unweighted Arnoldi on A (—), unweighted Arnoldi on B (- · -), S weighted Arnoldi on A (· · ·) and B (·····) and W weighted Arnoldi on A (- - -). Four nonconvergent lines in the lower right corner are for the Arnoldi method applied to the A^T matrix with no weighting and S, W, and W^2 weighting (from left to right). Calculated as a Ritz value. Light dotted line shows converged value.

300 cm^{-1}. The changes in behavior as the pressure was reduced were very similar to the changes observed as the $\langle \Delta E \rangle_{\text{down}}$ parameter was reduced. For example, the profile of the successive eigenvalue estimates with the number of iterations with $\langle \Delta E \rangle_{\text{down}} = 300\ \text{cm}^{-1}$ at a pressure of 0.65 Torr for all the 12 variants were very similar to those observed for $\langle \Delta E \rangle_{\text{down}} = 75\ \text{cm}^{-1}$ at a pressure of 6.5 Torr. That is, in the calculations for these two systems the number of iterations required for convergence and the route taken by the successive eigenvalue estimates on the way to convergence for each weighted Arnoldi method variant were similar. This observation applied equally to the smallest eigenvalue and larger ones, and is consistent with the traditional view that the eigenproblem becomes harder to solve as either the efficiency of the energy transfer or the pressure is reduced.

The Relations between Different Weightings

In the previous sections it was observed that the estimates for λ_1 coincided for successive iterations for three of the variants of the Arnoldi method trialed. It was stated that those three methods are intrinsically equivalent. In this section, the relationship between different combinations of similarity transformations (i.e., implicit weighting) and explicit incorporation of weighted inner products in the Arnoldi subspace projection method will be examined more closely. Before addressing the three methods highlighted in the last sections, it will be simpler to address another two variants that have a similar formal equivalence.

Consider the Arnoldi method weighted with W applied to the matrix A and unweighted Arnoldi applied to B. Let Q be the matrix comprised of the W-orthonormal basis vectors for $\mathcal{K}^{(m)}(A, \underline{q}_0)$ in the first case, and R be the matrix comprised of the orthonormal basis vectors for $\mathcal{K}^{(m)}(B, \underline{r}_0)$ in the second case. Q and R are then particular incarnations of the basis matrix V used in eqs. (22) through (28). Given that the eigenvectors of the two systems are related by eq. (12), it is appropriate to take seed vectors for the Krylov subspaces satisfying $\underline{r}_0 = S\underline{q}_0$. With this condition, the two subspaces being projected onto are related by

$$\mathcal{K}^{(m)}(B, \underline{r}_0) = S\mathcal{K}^{(m)}(A, \underline{q}_0). \tag{48}$$

It can be easily shown by an inductive argument (see Appendix A) that in fact the two bases are related by

$$R = SQ. \tag{49}$$

Equation (49) is a much stronger relation than eq. (48).

Furthermore, the projected matrices $H_{A(W)}$ and H_B are formally identical,

$$\begin{aligned} H_B &= R^T B R = Q^T S S A S^{-1} S Q \\ &= Q^T W A Q = H_{A(W)}. \end{aligned} \tag{50}$$

That is, the small projected problem to be solved, eq. (24), is the same for the two problems. The resultant eigenvector estimates for the untransformed eigenproblem, eq. (6), are given by

$$\underline{x} = Q\underline{c} \tag{51}$$

for the weighted problem in A [from eq. (22)] and

$$\underline{x} = S^{-1}\underline{y} = S^{-1}R\underline{c} = Q\underline{c} \tag{52}$$

for the unweighted problem in B [from eqs. (12), (22), and (49)]. Hence, barring errors introduced by roundoff, the eigenvector estimates are identical.

Thus, applying W weighting to the original eigenproblem yields a method formally equivalent to working with the symmetrised matrix B. In the numerical examples of the last sections, however, the eigenvalue estimates for these two variants were not coincident in either the smallest eigenvalue or

higher eigenvalue cases. This implies that, in the case of these two variants, roundoff error is playing a significant role in determining the solution.

By direct analogy with the bases R and Q, the bases produced by applying the Arnoldi method to A^T, to B weighted by W and to A weighted by W^2 should be related by the matrix S. These are the three variants claimed most noticeably in the previous sections to be equivalent. To formalize this take the W^2-orthonormal basis obtained by applying the Arnoldi method to the matrix A with an inner product weighted by W^2 as the columns of Q', the W-orthonormal basis obtained by applying the Arnoldi method to the matrix B with an inner product weighted by W as the columns of T and the basis obtained by applying the unweighted Arnoldi method to the matrix A^T as the columns of U. In these cases the seed vector for the Krylov subspace is taken as $\underline{q}'_0$ for Q', $S\underline{q}'_0$ for T and $W\underline{q}'_0$ for U, as appropriate by virtue of eqs. (12) and (46). Inductive proofs very similar to that presented in Appendix A can again be used to show that

$$U = ST = WQ'. \tag{53}$$

In this case arguments similar to eq. (50) still apply, namely that

$$\begin{aligned} H_{A^T} &= U^T A^T U = Q'^T WWAW^{-1}WQ' \\ &= Q'^T W^2 AQ' = H_{A(W^2)} \end{aligned} \tag{54}$$

and

$$\begin{aligned} H_{B(W)} &= T^T WBT = Q'^T SWSAS^{-1}SQ' \\ &= Q^T W^2 AQ = H_{A(W)}, \end{aligned} \tag{55}$$

so that the projected matrices are once again identical. Indeed, these proofs can be extended to show wide classes of formally equivalent partitionings of the weighting between the matrix and the inner product. A WIP Arnoldi method with an inner product weighted by S^{2m} on the matrix $S^n AS^{-n}$ is formally equivalent to all other similar methods for which the quantity $m + n$ is the same, differing only in accumulated roundoff error. It appears from the results presented in Figure 3 that the critical roundoff error associated with the $m + n = 2$ and $m + n = 3$ cases is much more well behaved than in the $m + n = 1$ case.

Summary

Figures 3 and 7 demonstrate conclusively that the WIP Arnoldi method can successfully find the troublesome smallest eigenpair of the EGME—even at temperatures and pressures where this eigenvalue is extremely small. For this purpose, the most effective weighting of those tested was that involving the inverse of the Boltzmann equilibrium distribution squared. This weighting can be incorporated into the calculations in several different ways: either explicitly, by applying WIP Arnoldi to the rate matrix A with the full W^2 weighting, or through equivalent formulations that partition the weighting between a WIP and a similarity transformation of the matrix. The superior performance of this particular weighting for the calculation of the lowest eigenpair can be rationalized by noting that it effectively regularizes the sought-after eigenvector by allowing one to solve for the left eigenvector of A (or the corresponding right eigenvector of A^T), which has elements of order 1. In contrast, the right eigenvector of A—and that of the symmetric B—has elements that decrease exponentially towards the high-energy elements, which leads to catastrophic loss of precision when attempting to compute these right eigenvectors with subspace projection methods.

It appears, however, that this weighting can be at the cost of the convergence of the higher eigenpairs. Indeed, the most consistent convergence for the cases of λ_3, λ_6, and λ_9 were generally achieved by the unweighted, untransformed method on the rate matrix A.

The situation is summarized by the following table. Each box in this table corresponds to a WIP Arnoldi variant, with the weighting matrix specified on the left and the matrix the Arnoldi method was applied to along the top. A bold "**L**" in a box indicates that that variant successfully calculated the smallest eigenvalue and corresponding eigenvector in all cases, while a bold "**H**" indicates that the variant successfully converged to larger eigenvalues. Nonbold entries indicate that there were some problems associated with the method for that regime, such as slow convergence, instability, or some other caveat as discussed in the text.

	A	B	A^T
I	**H**	**H**	H **L**
S	**H**	H L	H L
W	**H**	H **L**	L
W^2	H L	L	

Particularly interesting regions of this table for the present purposes are areas where the two convergence regimes (smallest and larger eigenvalues, indicated by "L" and "H") overlap. This occurs mostly around a weighting of W^2 applied to the A matrix, or equivalently unweighted Arnoldi on A^T.

This level of weighting is far from ideal, however, with the larger eigenvalues not converging for matrices derived from the narrow exponential-down kernels. Applying a higher weighting than this leads to slow convergence for the smallest eigenvalues and loss of convergence for the larger ones, whereas with significantly lower weighting the numerical difficulties and lack of precision return, destroying any convergence for the smallest eigenpair.

Interesting cases around this critical weighting line are the weightings by S applied to the B and A^T matrices. The B case is applying slightly less weight (equivalent to a $W^{1.5}$ weighting on A), whereas the A^T case is applying slightly more (equivalent to a $W^{2.5}$ weighting on A). With the $W^{2.5}$ weighting case, the convergence is slowed and a measure of stability is lost (as evidenced by the nonsmooth behavior of the eigenvalue estimates as a function of iteration for this variant as presented in Fig. 3). The lower $W^{1.5}$ weighting, on the other hand, shows superior convergence behavior for the eigenvalue coupled with a loss of sensitivity for high-energy, very small elements of the eigenvector.

Certain variants of the weighted Davidson method provided performance far superior to that of the weighted Arnoldi method for finding the smallest eigenpair, converging after just one iteration in one case. However, the Davidson method tended to be far more unstable than the Arnoldi method. The Davidson method also failed to produce any of the higher eigenpairs, which was one of the main aims of this work.

In conclusion, the weighted inner product approach introduced here for the solution of the EGME reveals that subspace projection methods can be effectively utilized for thermal unimolecular rate calculations under conditions of low temperature and pressure. This is a new development in master equation capabilities. It opens up the potential for computational modeling of more general problems involving transient relaxation under low-temperature conditions where all extant numerical methods fail, for example, product branching ratios in chemical activation reactions. The WIPSP approach introduced in this work will need further development and/or modification to achieve this goal, however, and work along these lines is continuing.

Acknowledgments

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Appendix A: Proof that $R = SQ$

Presented here is the inductive proof that the Arnoldi basis matrices R and Q defined in the text obey $R = SQ$.

Consider first the Arnoldi iteration applied to the problem $A\underline{x} = \lambda\underline{x}$ with an inner product weighted by the diagonal matrix W. The $(i+1)$th basis vector is calculated as

$$\underline{q}_{i+1} = \frac{A\underline{q}_i - \sum_{j=1}^{i}\langle \underline{q}_j, A\underline{q}_i\rangle_W \underline{q}_j}{\|A\underline{q}_i - \sum_{j=1}^{i}\langle \underline{q}_j, A\underline{q}_i\rangle_W \underline{q}_j\|_W} = \frac{A\underline{q}_i - \sum_{j=1}^{i}(\underline{q}_j^T WA\underline{q}_i)\underline{q}_j}{\|SA\underline{q}_i - \sum_{j=1}^{i}(\underline{q}_j^T WA\underline{q}_i)S\underline{q}_j\|}, \quad \text{(A.1)}$$

where we have used the fact that $\|\underline{v}\|_W = \underline{v}^T W\underline{v} = \underline{v}^T SS\underline{v} = \|S\underline{v}\|$. The corresponding expression for the basis generated from $B\underline{y} = \lambda\underline{y}$ is

$$\underline{r}_{i+1} = \frac{B\underline{r}_i - \sum_{j=1}^{i}\langle \underline{r}_j, B\underline{r}_i\rangle \underline{r}_j}{\|B\underline{r}_i - \sum_{j=1}^{i}\langle \underline{r}_j, B\underline{r}_i\rangle \underline{r}_j\|}. \quad \text{(A.2)}$$

Noting that $B = SAS^{-1}$ and assuming that $\underline{r}_i = S\underline{q}_i$ gives

$$\underline{r}_{i+1} = \frac{SA\underline{q}_i - \sum_{j=1}^{i}(\underline{q}_j^T S^2 A\underline{q}_i)S\underline{q}_j}{\|SA\underline{q}_i - \sum_{j=1}^{i}(\underline{q}_j^T S^2 A\underline{q}_i)S\underline{q}_j\|} = S\left(\frac{A\underline{q}_i - \sum_{j=1}^{i}(\underline{q}_j^T WA\underline{q}_i)\underline{q}_j}{\|SA\underline{q}_i - \sum_{j=1}^{i}(\underline{q}_j^T WA\underline{q}_i)S\underline{q}_j\|}\right) = S\underline{q}_{i+1}. \quad \text{(A.3)}$$

Given that $\underline{r}_0 = S\underline{q}_0$, one has

$$\underline{q}_1 = \frac{\underline{q}_0}{\|\underline{q}_0\|_W} = \frac{\underline{q}_0}{\underline{q}_0^T W\underline{q}_0} \quad \text{(A.4)}$$

so that

$$\underline{r}_1 = \frac{\underline{r}_0}{\|\underline{r}_0\|} = \frac{S\underline{q}_0}{\underline{q}_0^T S^2\underline{q}_0} = S\underline{q}_1, \quad \text{(A.5)}$$

and, hence, the assumption that $\underline{r}_i = S\underline{q}_i$ holds for $i = 1$. Then by induction, one has (column-wise) $R = SQ$. Similar arguments are easily constructed to show that $U = ST = WQ'$.

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